A103 The Differentiation of Kerosene Samples by Target Compound Ratio Analysis

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The goal of this presentation is to present initial results of a method developed to differentiate kerosene samples and residues from fire debris by Gas Chromatography/Mass Spectrometry (GC/MS) using target compound ratio analysis. This method is an extension of a method developed for the differentiation of gasoline samples as neat liquids and fire debris residues. The ultimate goal of both projects is the development of a uniform statistical method to establish the degree of similarity between any two ignitable liquid residues in fire debris analysis.

This presentation will impact the forensic science community by providing methodology and a statistical basis for declaring a similarity between any two kerosene samples as required by the courts and the recent National Academy of Sciences report.

Although gasoline is the number one ignitable liquid used as an accelerant in arson cases, kerosene is number two in much of the United States. Similar products classified as middle petroleum distillates (MPD) by the American Society for Testing and Materials (ASTM) E1618 method are also common due to their availability as charcoal lighters, paint thinners, and solvents. Classification of ignitable liquids according to the E1618 classification scheme can readily identify the ignitable liquid residue as a gasoline, MPD, or kerosene; however, comparing two samples (i.e. residue from fire debris to residue from a suspect's clothing) to determine if they are from the same source is much more problematic. This research was undertaken to provide the analytical and statistical basis for making such a determination.

Target compound ratio analysis is applied to high resolution GC/MS data utilizing the peak area ratio of sequentially eluting key compounds. Compounds eluting from a non-polar polydimethylsiloxane column elute primarily in boiling point order. Therefore, two compounds eluting with similar retention times will have similar boiling points and thus similar evaporation rates during a fire. Although the two compounds may decrease in overall concentration with increasing evaporation, their peak ratio will see little change. This allows comparison between samples with different amounts of evaporation. Kerosene, unlike gasoline, is a simple distillation product from crude oil and should be strongly related to the petroleum from which it was distilled. The relative concentrations of the key components in kerosene from a refinery will often change daily because of the variety of sources that distribute crude oil. This variation in concentration can provide sufficient variability for comparison between individual kerosenes. A number of compounds have been identified by the petroleum industry for crude oil typing and for matching a given crude oil source with environmental contamination from a tanker

spill or pipeline release. The preliminary work completed has identified thirty possible ratios for the comparison between kerosene samples. The target compounds selected have adequate concentrations in the kerosene samples, which allows for reproducible ratios between injections, as well as significant variation between kerosene samples from different sources. Two commonly used metrics for crude oil typing are odd/even predominance of normal hydrocarbons and the pristine/phytane ratio. Pristine and phytane are both in low amounts in kerosene (near the upper boiling point limit); therefore, this ratio was found to be too variable within a given sample to be useful. Odd/even predominance showed good reproducibility within samples, but showed little statistical difference between the first set of kerosene samples, thus making the ratio not applicable for this purpose. The relative amount of normal hydrocarbons to iso- and cyclo-paraffins does show both reproducibility and statistical difference between kerosene samples as neat liquids. Burn tests and evaporated samples will be presented to show the robustness of these
compound ratios under a variety of conditions and substrates.

Comparison of MPD will be presented with a similar set of target compounds for comparison and differentiation of this ignitable liquid class. A database of gasoline, MPD, and kerosene analyses is being developed from a large number of samples from a variety of sources. This database will be necessary to establish the statistical criteria for declaring two samples similar with a probability of error.

Kerosene, Target Compound Ratios, Fire Debris Analysis

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